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INFLUENCE OF JET FUEL ON PERMEATION AND FLAMMABILITY
CHARACTERISTICS OF GRAPHITE EPOXY COMPOSITES

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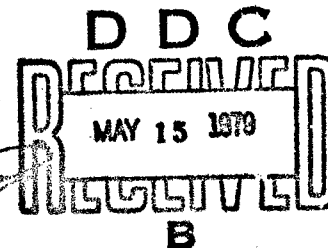
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INTRODUCTION

The increased use of graphite epoxy composite materials in the design of future Navy aircraft has generated the need for assuring the durability and safety of these materials during service life when subjected to conditions found in the aircraft environment. The high strength/low mass ratio of the graphite epoxy composite (GR/E) make its use especially attractive as a replacement material for fuel tanks. Since the composites are made of specially oriented graphite fibers and epoxy resin, the question of possible flammability or permeability when exposed to jet fuel needed to be addressed. A laboratory investigation was funded by the Naval Air Systems Command, and work was carried out under AIRTASK No. A03V-0000/001B/3F41-400-000 by the Materials Characterization Section of the Aircraft and Crew Systems Technology Directorate (ACSTD).

RESULTS

Studies of the permeability of JP-5 aircraft fuel through laboratory prepared specimens of graphite epoxy composites showed no detectable permeation using the techniques of infrared and nuclear magnetic resonance spectroscopy. In the flammability tests, all samples were found to be self extinguishing. The fuel immersion tests all exhibited a trend of slow weight gain over time, approximately 9×10^{-8} grams per square centimeter of area per hour.

CONCLUSIONS

The results of the fuel permeation tests indicate that there should be no major problem with fuel diffusion through graphite epoxy composite material which would be used as a fuel tank liner. The flammability tests completed at this time indicate that the graphite epoxy composite should not pose a serious fire problem in the presence of aircraft fuel. The slow rate at which fuel is absorbed by the composites in the immersion tests indicate that gross uptake of fuel by a fuel tank liner would not be predicted.

RECOMMENDATIONS

Flammability tests on 20 ply specimens are planned and will be carried out when fabrication of the samples is completed. This will give a more representative idea of the behavior of the relatively thick liner of a fuel tank.

The weight gain observed in the fuel immersion tests has been assumed to result primarily from the absorption of fuel, but almost certainly results to some extent from the absorption of water present in the fuel, water being more readily absorbed than fuel by the graphite epoxy composite materials. The best method for determining how much weight gain is due to fuel or water is to subject specimens to thermogravimetric analysis after immersion studies

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are completed. The resulting data would show two distinct weight losses corresponding to fuel and water. Results from samples which have undergone various water pretreatments before immersion in fuel would be compared with those with no water pretreatment.

Also recommended would be the microscopic examination of the graphite epoxy composites after permeation and immersion tests. Certain color changes have been observed on the surfaces of some of the specimens. It would be advantageous to see what other surface changes and degradations have been produced. Cross sectional analysis may indicate the depth of fuel and/or water permeation, as well as the depth of surface degradation if it occurs.

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DISCUSSION

BACKGROUND

In November of 1977, a proposal was approved for ACSTD to begin a laboratory investigation. The objective was to provide information on the permeability of jet aircraft fuels through laboratory prepared sections of graphite epoxy composites, the flammability of the material either alone or enhanced by the presence of jet fuel, the behavior of the material when immersed in fuel as evidenced by weight change, and any visible degradation of the composite by any facet of the testing.

To this end, a program of laboratory testing was devised. The permeation testing would be monitored using two spectroscopic techniques - infrared (IR) and nuclear magnetic resonance (NMR), both of which are very sensitive to the molecular structure of organic compounds. Both techniques are capable of detecting very low concentrations of hydrocarbons, of which jet fuel is composed. Special cells had to be designed to sandwich a graphite epoxy test specimen of 5 or 10 ply between a monitoring cell and a cell filled with JP-5 fuel (Figures 1 and 2). The flammability tests were carried out in accordance with Federal Test Method Standard Number 406, Method 2021, on 5 ply specimens, with and without prior exposure to JP-5 fuel. The immersion tests were carried out on 5, 10, 20, and 60 ply specimens under various conditions of immersion in JP-5, some involving preconditioning in water with or without subsequent drying of the specimens.

PERMEATION STUDY BY INFRARED SPECTROSCOPY

The infrared spectrophotometer is a very sensitive instrument which can detect minute amounts of hydrocarbons, of which JP-5 is composed, and can even detect fuel in the vapor state, the detectable limit of fuel vapor in a 10 cm infrared cell being approximately 30 ppm. The sample cell which was designed and fabricated to hold the graphite epoxy specimens consisted of a 10 cm infrared transparent cell which had two ports at which two specimens were sandwiched between the cell and a sealed fuel reservoir, all held in place with fuel resistant gaskets and spring clamps. The 10 cm cell was carefully cleaned before the samples and fuel chambers were attached, so that any characteristic infrared bands that might be detected during testing would be due to fuel permeating through the test specimens into the cell. This entire unit was placed in the spectrophotometer periodically to see if any JP-5 vapor could be detected.

Initial studies were carried out on 5 ply specimens at room temperature. The infrared spectrum immediately gave positive indications of JP-5. However, the 5 ply panels were so thin that diffusion through small cracks in the sample was suspected as the cause since the specimens were fabricated in the zero direction, which makes them very susceptible to mechanical cracking. To determine if this was the case, the cell was disassembled and new 5 ply specimens were used. This time no fuel bands were observed in the spectra. The test was continued for 500 hours, and no permeation of fuel was detected.

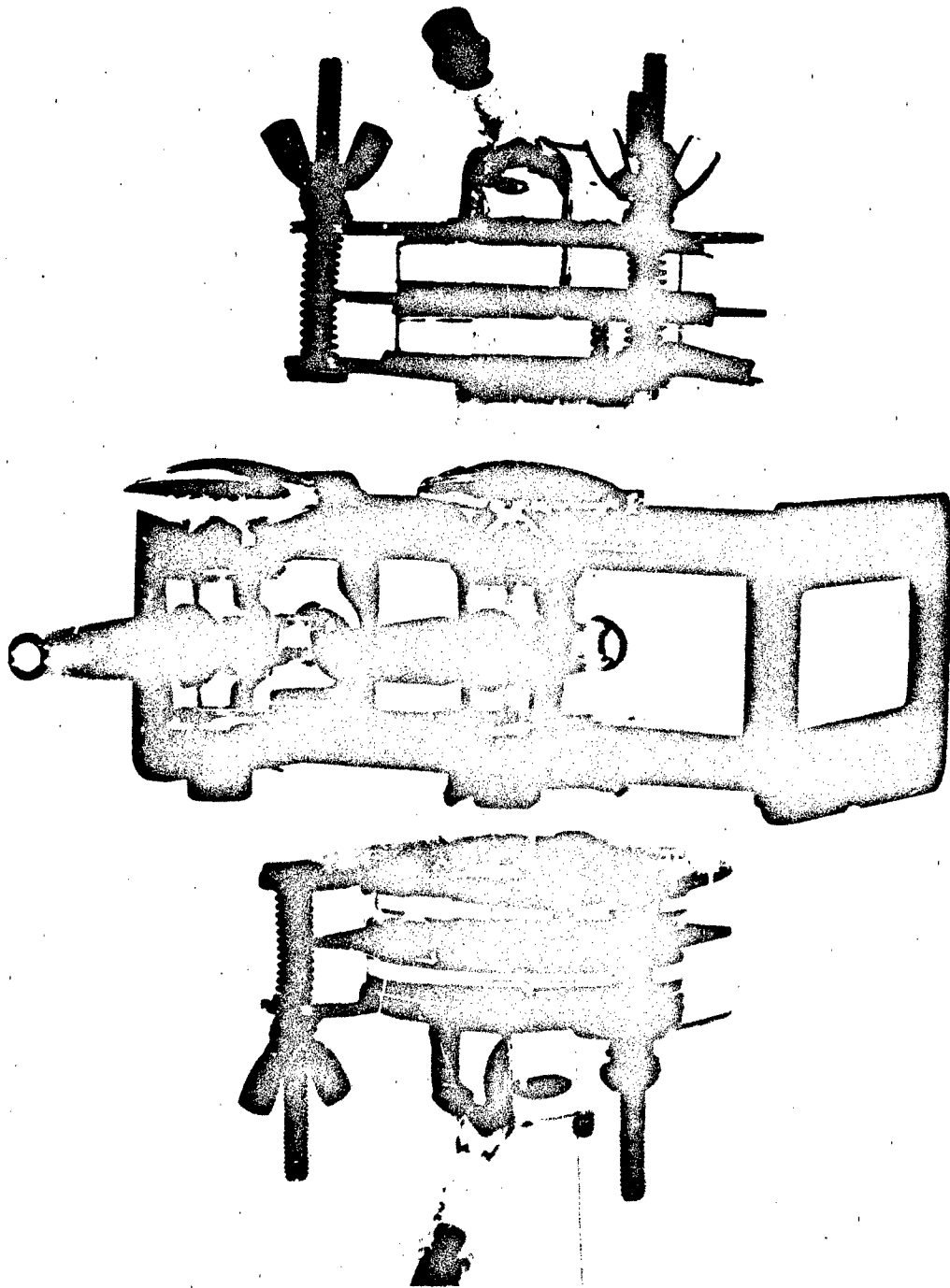


FIGURE 1. INFRARED PERMEATION CELL

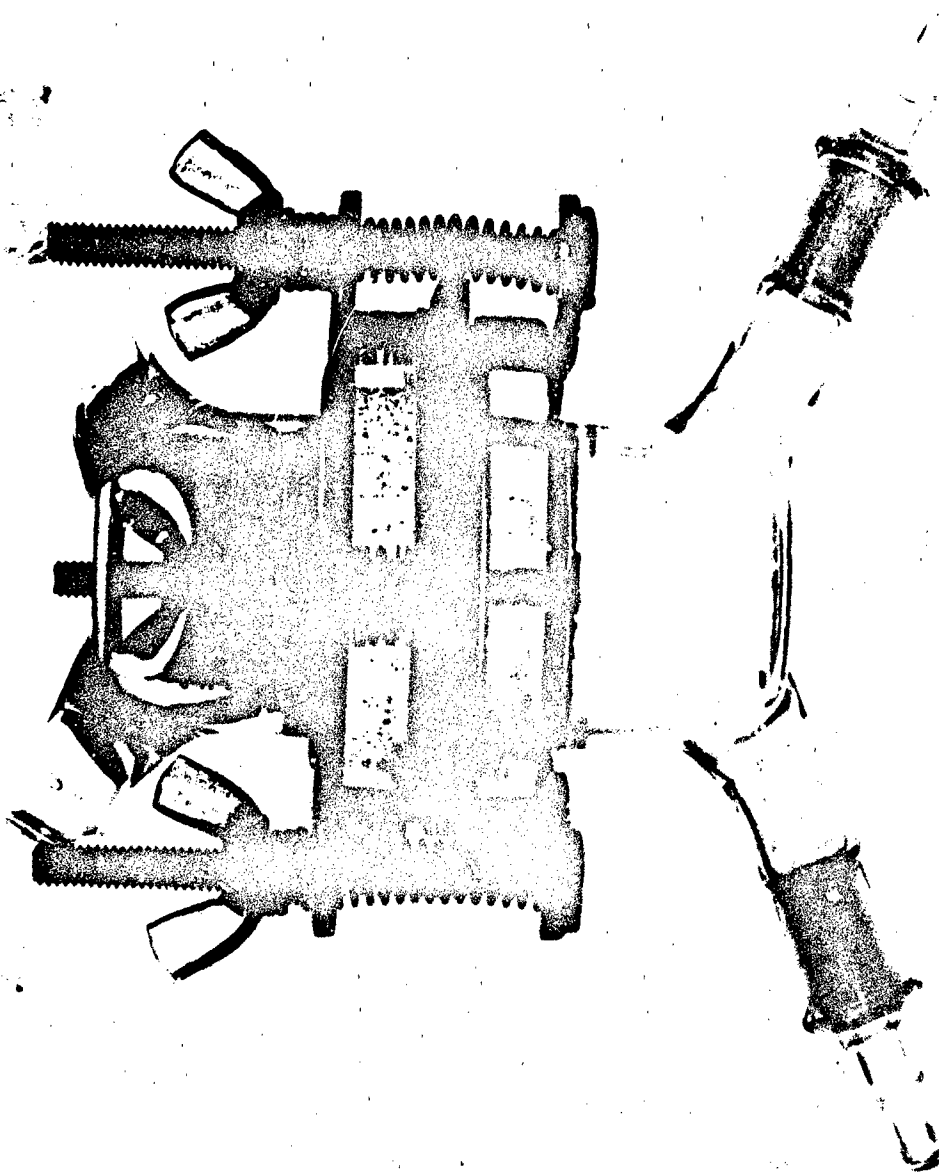


FIGURE 2. NUCLEAR MAGNETIC RESONANCE PERMEATION CELL

10 ply specimens were then placed in the cell. It was first monitored at room temperature for 400 hours, during which no fuel permeation was detected. The cell was then placed in a sand bath and kept at 160°F. It was periodically removed to determine the infrared spectrum. After 700 hours no fuel permeation had been detected (Table I).

TABLE I. FUEL PERMEATION RESULTS

INFRARED SPECTROSCOPY

<u>Ply</u>	<u>Condition</u>	<u>Duration of Test (Hours)</u>	<u>Amount of JP-3 Fuel Present</u>
5	Room temperature	500	None detected
10	Room temperature	400	None detected
10	160°F	700	None detected

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

<u>Ply</u>	<u>Conditions</u>	<u>Duration of Final Test Interval (Hours)</u>	<u>Amount of JP-5 Fuel Present</u>
10	Room temperature No water added	1350	None detected
10	Room temperature 1% water added	500	None detected
10	120°F No water added	500	None detected
5	Room temperature No water added	1550	None detected
5	Room temperature 1% water added	1550	None detected
5	120°F No water added	50*	None detected

* Cell cracked under heating, test discontinued.

PERMEATION STUDY BY NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

In order to study the permeation of aircraft fuel by NMR, a preliminary calibration curve was constructed from known amounts of fuel in deuterated chloroform (CDCl_3). Permeation cells were designed and specially constructed for the tests. A graphite epoxy specimen was sandwiched between two glass chambers and secured in place using fuel resistant gaskets and a spring loaded clamp. One chamber of the cell was filled with JP-5 aircraft fuel and capped. The other reservoir was left empty and capped. The test cell was oriented in such a way that the fuel filled chamber was on top, so that permeation, if it should occur, would be aided by gravity. The monitoring of the test cells for fuel permeation took place in the following way. The empty side of the test chamber was rinsed with 0.5 ml of CDCl_3 solvent, which would dissolve any fuel that had permeated through the graphite epoxy specimen. This was then transferred to an NMR sample tube, placed in the NMR spectrometer and the spectrum observed for evidence of JP-5. This method of testing was not cumulative in time as was the infrared method, but instead the test interval was the elapsed time between solvent washings. Starting with an initial one day interval, the intervals were gradually increased, with final measurements made after intervals up to 1550 hours (Table I.)

Two sets of graphite epoxy specimens were tested by NMR: 5 ply and 10 ply. The conditions under which they were tested included room and elevated temperatures, JP-5 only and JP-5 with 1% water added. No permeation was detected by NMR in any of the test cells.

FLAMMABILITY TEST

The flammability of the graphite epoxy composites was of prime concern considering its proposed use in aircraft fuel tanks. The tests were performed on thirty 5 ply specimens, 12.7 cm long by 1.3 cm wide. Ten specimens were immersed in JP-5 for 24 hours and tested while wet. Ten specimens were immersed in JP-5 for 24 hours, then air dried for 24 hours before testing. Ten specimens were tested with no exposure to fuel. The samples were tested in accordance with Federal Test Method Standard Number 406, Method 2021, reference (a). Flammability tests were conducted in a laboratory hood with the exhaust fan left off. The test equipment was set up as shown in Figure 3, with a ring stand, clamp, wire gauze, and bunsen burner. Each specimen was marked at 2.5 cm and at 10.2 cm from the flame end. The specimen was supported with its longitudinal axis horizontal and its transverse axis inclined at 45 degrees to the horizontal. The blue flame tip from the bunsen burner was placed in contact with the specimen for 30 seconds and then removed. All of the 5 ply specimens failed to burn up to the 2.5 cm mark, and according to the conditions of Method 2021, were found to be self-extinguishing. On those specimens tested with wet JP-5 on their surfaces, the fuel seemed to be driven away from the flame front, and it appeared that the fuel did not contribute to the extent of burning of the specimen.

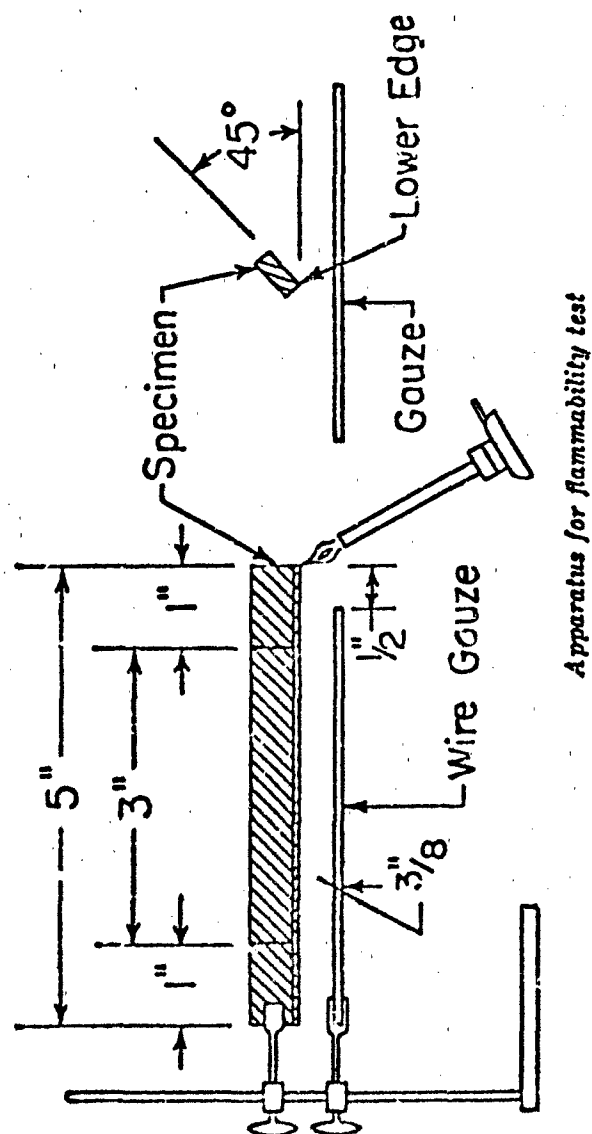


FIGURE 3. APPARATUS FOR FLAMMABILITY TEST

IMMERSION STUDY

Four different types of immersion studies were carried out in this laboratory. Specimens of 5, 10, 20 and 60 ply were fabricated for these tests, all having the graphite fibers oriented in the zero direction. The test specimens were cut from larger sheets using a diamond blade saw so that minimum fiber damage would be produced during sample preparation. The edges of all specimens were sealed with epoxy resin in accordance with MIL-S-8802D (Class B-2) to prevent fuel absorption into the composite through the edges instead of through the ply thickness. After sealing, the specimens were allowed to air dry at room temperature for 96 hours, then were cured at 52°C for 48 hours, after which they were cooled in a dessicator and weighed.

A. Specimens immersed in JP-5 only.

The dimensions of the specimens used were 2.5 cm x 5.0 cm (total surface area of 25 cm²). After the sealing and weighing procedure, three specimens each of 5, 10, 20, and 60 ply were completely immersed in containers of JP-5 fuel (Figure 4). At 24 hours, the specimens were removed from the immersion dish, blotted in a uniform manner, and reweighed. Subsequent weighings were made at various time intervals until the test was terminated at 4800 hours for 5 and 10 ply specimens and at 12,400 hours for 20 and 60 ply specimens. Plots of the average weight gains for the different plies over the first 3500 hours are shown in Figures 5 to 8. All specimens showed a trend of gradual weight gain. Although the 5 ply specimens showed somewhat less absorption than the others, the 10, 20, and 60 ply specimens all exhibited similar weight gains, indicating that absorption seemed to be more a function of surface area than thickness of the plies, and on the order of 9.0×10^{-8} g/cm² hr, as shown in Table II.

B. Specimens immersed in water only.

Four specimens, each of 5, 10, and 20 ply, were used for this test. All had dimensions of 4.0 cm x 5.0 cm (total surface area of 40 cm²), and were sealed and weighed as were those in the A group. The samples were then immersed in distilled water. The weight changes over time were recorded just as in the previous group until the tests were terminated at 1800 hours. The tests showed that water is much more readily absorbed by the composite material than is JP-5, on the order of 1.5×10^{-6} g/cm² hr. Again, absorption was gradual over time, but the test showed that the 20 ply samples gained more weight than 10 ply, which in turn gained more weight than 5 ply specimens, indicating that absorption may be a function of the number of plies as well as surface area for water absorption.

C. Samples pretreated in water 1800 hours prior to immersion in JP-5.

1. Two samples each of 5, 10, and 20 ply specimens from the B group (immersed in water for 1800 hours) were air dried for 92 hours, weighed, and then immersed in JP-5. Weight changes were followed for 9600 hours. For the first 5000 hours little gain in weight was observed, and some samples

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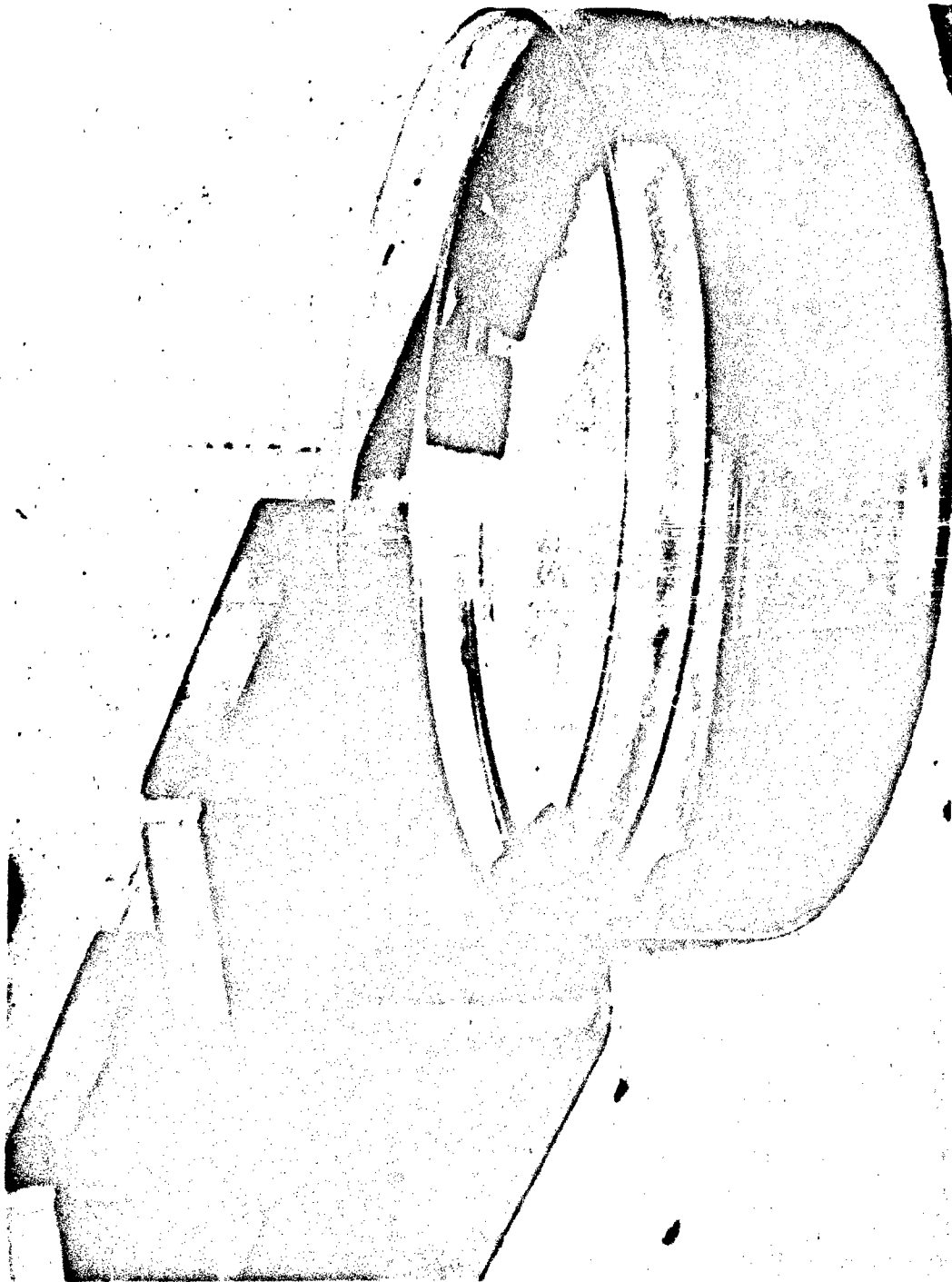


FIGURE 4. APPARATUS FOR FUEL IMMERSION STUDY

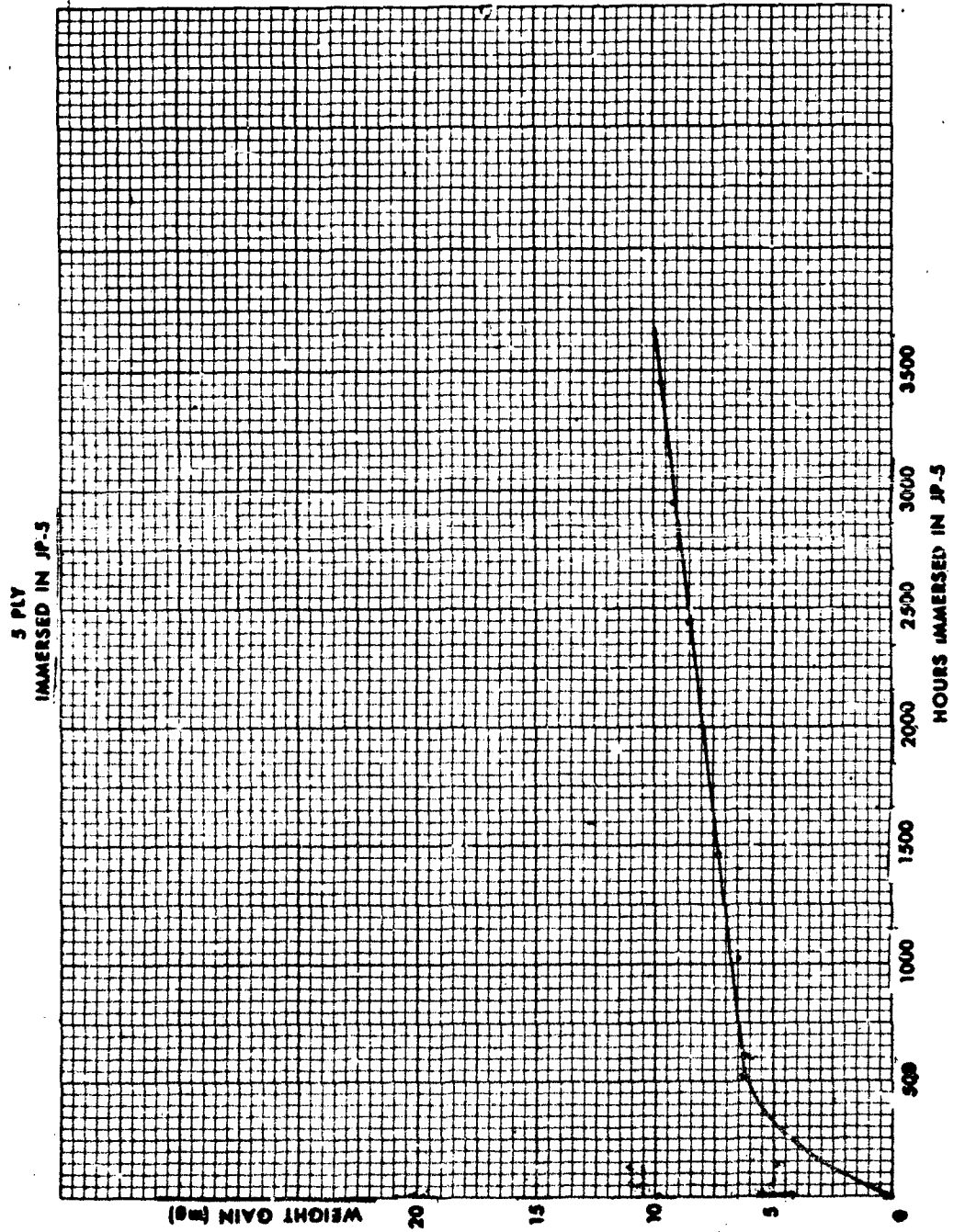


FIGURE 5. 5 PLY GR/E IMMERSSED IN JP-5

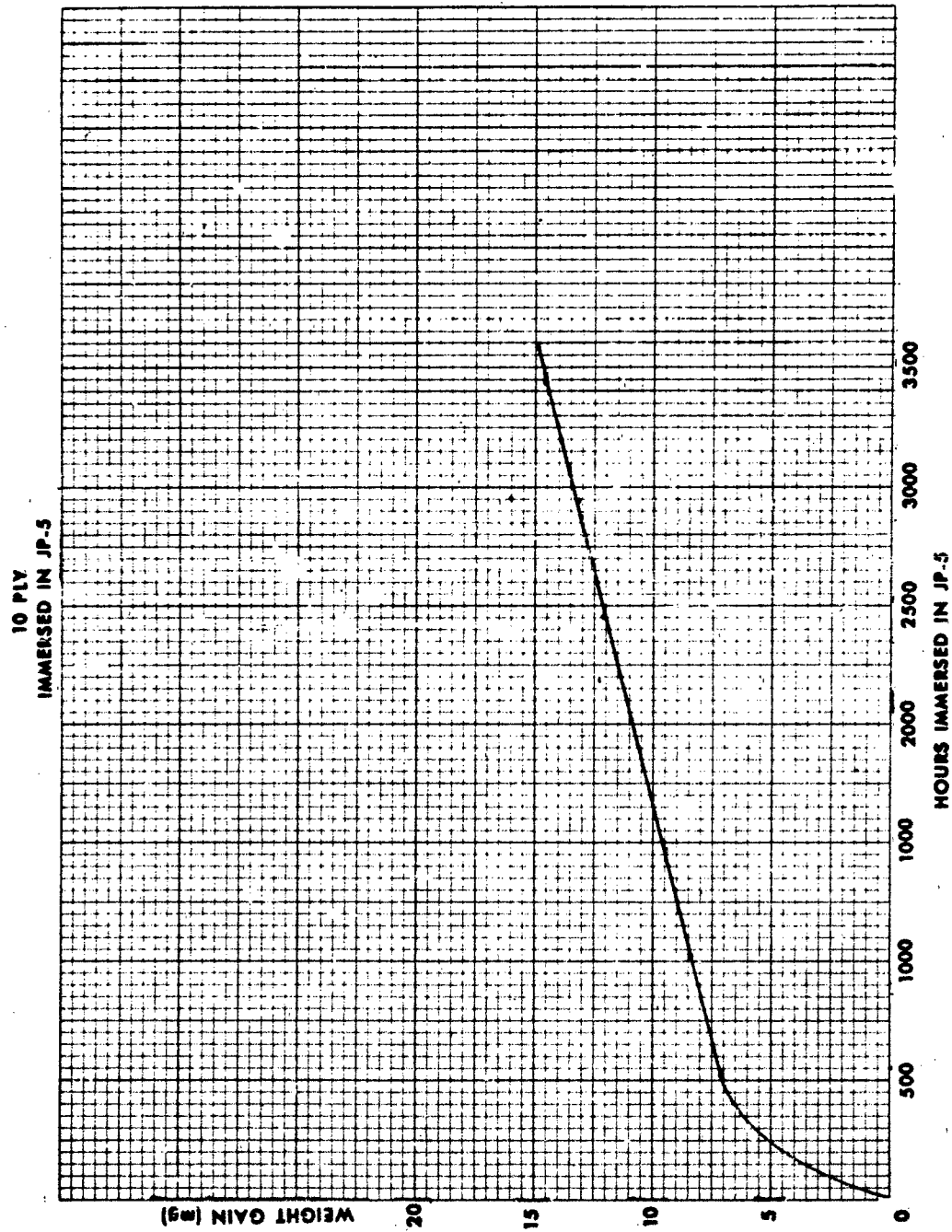


FIGURE 6. 10 PLY GR/E IMMERSED IN JP-5

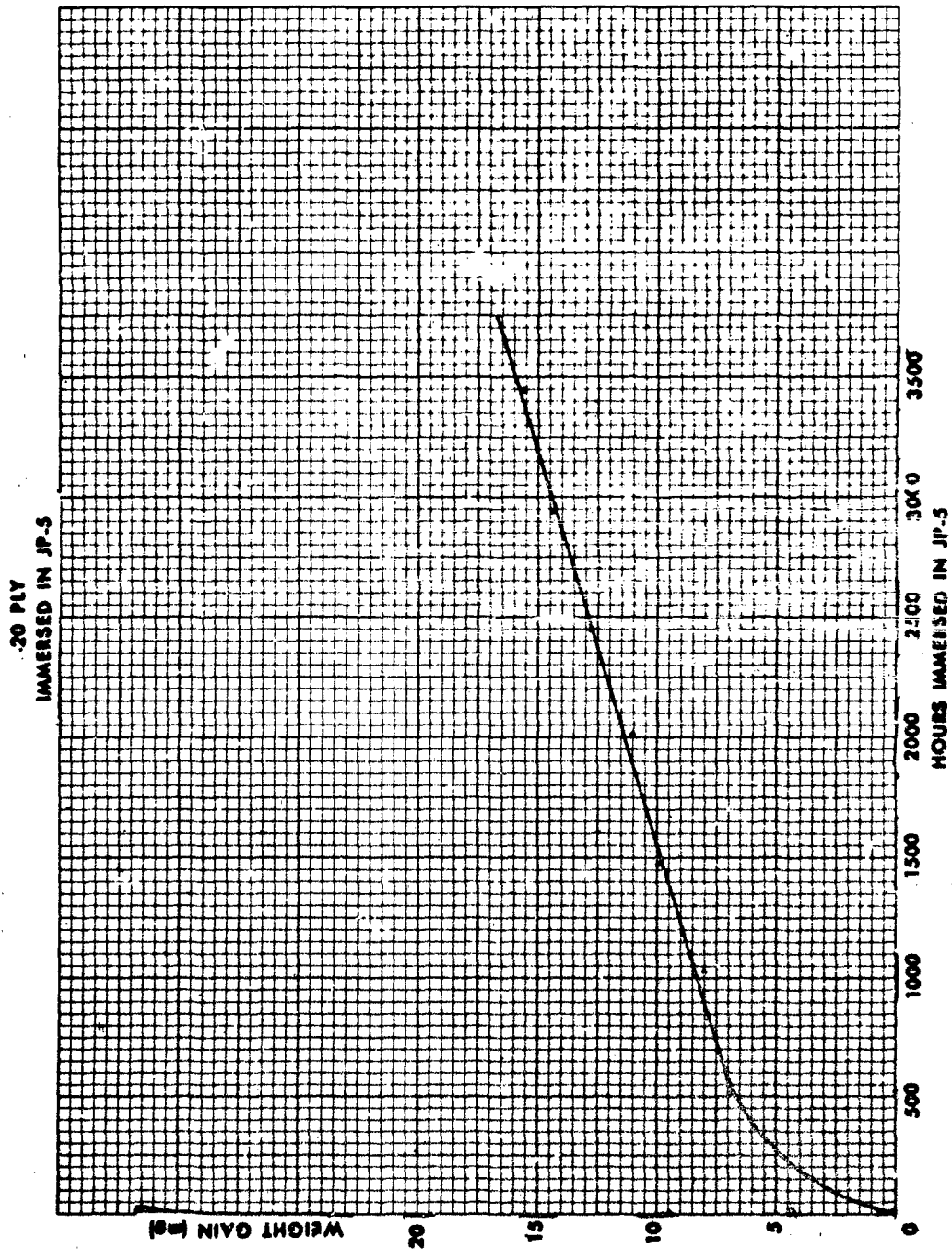


FIGURE 7. 20 PLY CR/E IMMERSSED IN JP-5

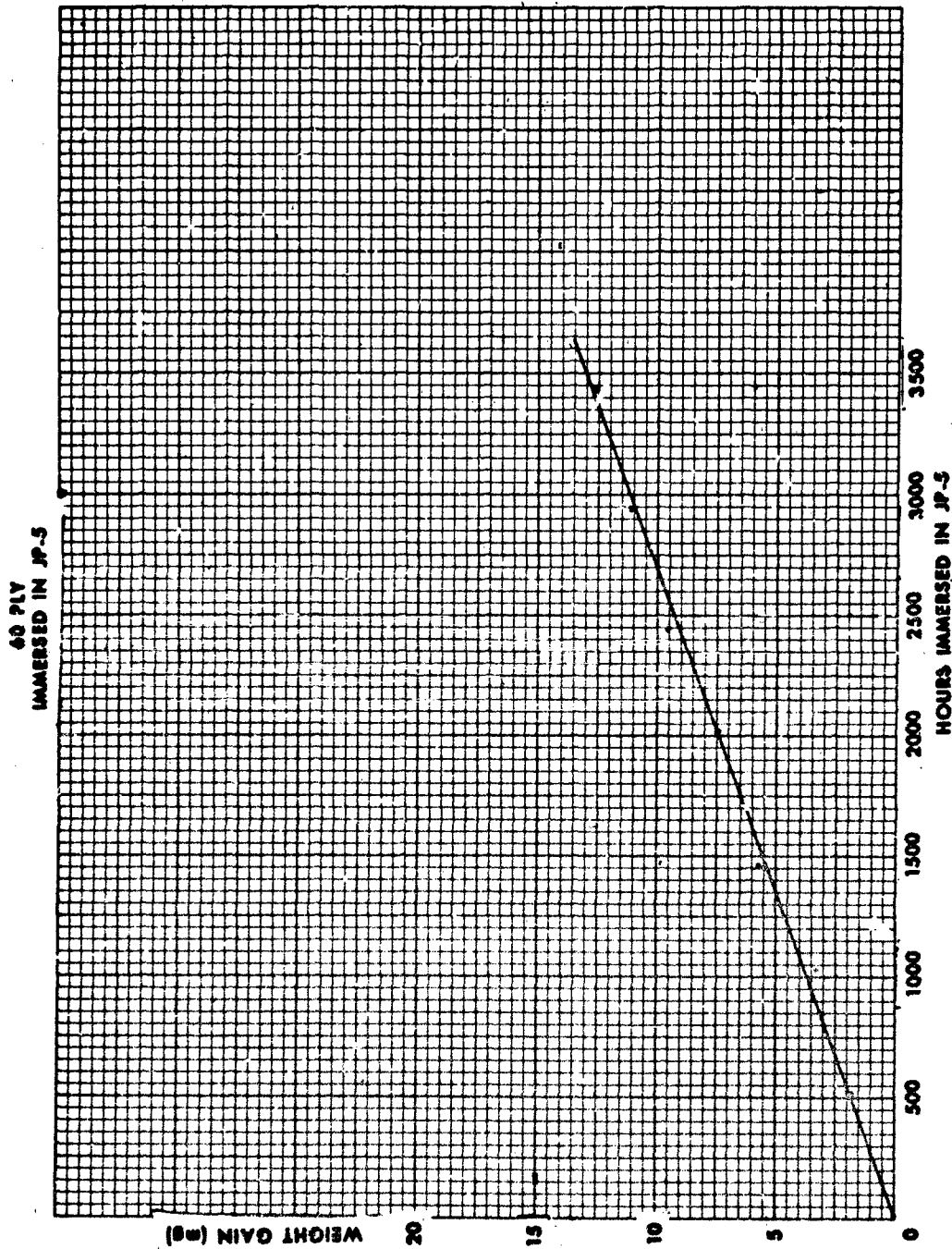


FIGURE 8. 60 PLY GR/E IMMERSED IN JP-5

showed weight loss (assumed to be loss of water from the pretreatment). After 5000 hours, however, the samples began to behave like the untreated samples immersed in fuel (A group), showing gradual increase in weight over time. The 5 and 10 ply samples showed similar weight gains when the test was terminated. The weight gain for the 20 ply specimens was somewhat higher.

2. Two samples each of 5, 10, and 20 ply were removed from the 1800 hour water immersion. The specimens were blotted dry and immediately immersed in JP-5, with no air drying. These specimens behaved in a manner grossly different from those in C.1. All samples showed an initial large and rapid weight loss, with the 20 ply losing more than the others. This weight loss continued until about 1500 hours, after which a slow, steady weight gain began which continued until the test was terminated at 9600 hours.

D. Samples pretreated in water 24 hours prior to immersion in JP-5.

The dimensions of the specimens used in this test were 2.5 cm x 5.0 cm (total surface area of 25 cm²). They were sealed and weighed as previously described, then soaked in distilled water for 24 hours. The samples were then blotted dry and immediately immersed in JP-5 (as in C.2.). The samples all showed a gradual weight increase until the test was terminated at 8600 hours. This behavior was similar to the group A samples which had no water pretreatment, and dissimilar to group C.2., although the only difference in pretreatment was the length of the water soak. Plots of the average weight gains for the different plies over the first 8000 hours are shown in Figures 9 to 11, and the weight gains at 5000 hours and 8616 hours are listed in Table II.

ADDITIONAL TESTS

The original water content of the JP-5 fuel used in the previous tests was determined to be 90 parts per million.

In order to obtain some information about the pore structure of the graphite epoxy composites, tracer studies were initiated using radioactive sodium and chloride ions in aqueous solution. The test cell consisted of two chambers separated by a 3 ply graphite epoxy specimen. One chamber held the salt solution containing the radioactive ions. The other was filled with distilled water. Permeation of the barrier was determined by the detection of radioactive ions in the distilled water side. The tracer studies were carried out for 5850 hours. The smaller sodium ions showed a slow rise in concentration from the outset of the test. The larger chloride ions showed no measurable concentration until 5000 hours, and then showed only a minimal concentration, indicating that the pore structure of the graphite epoxy composites is very small.

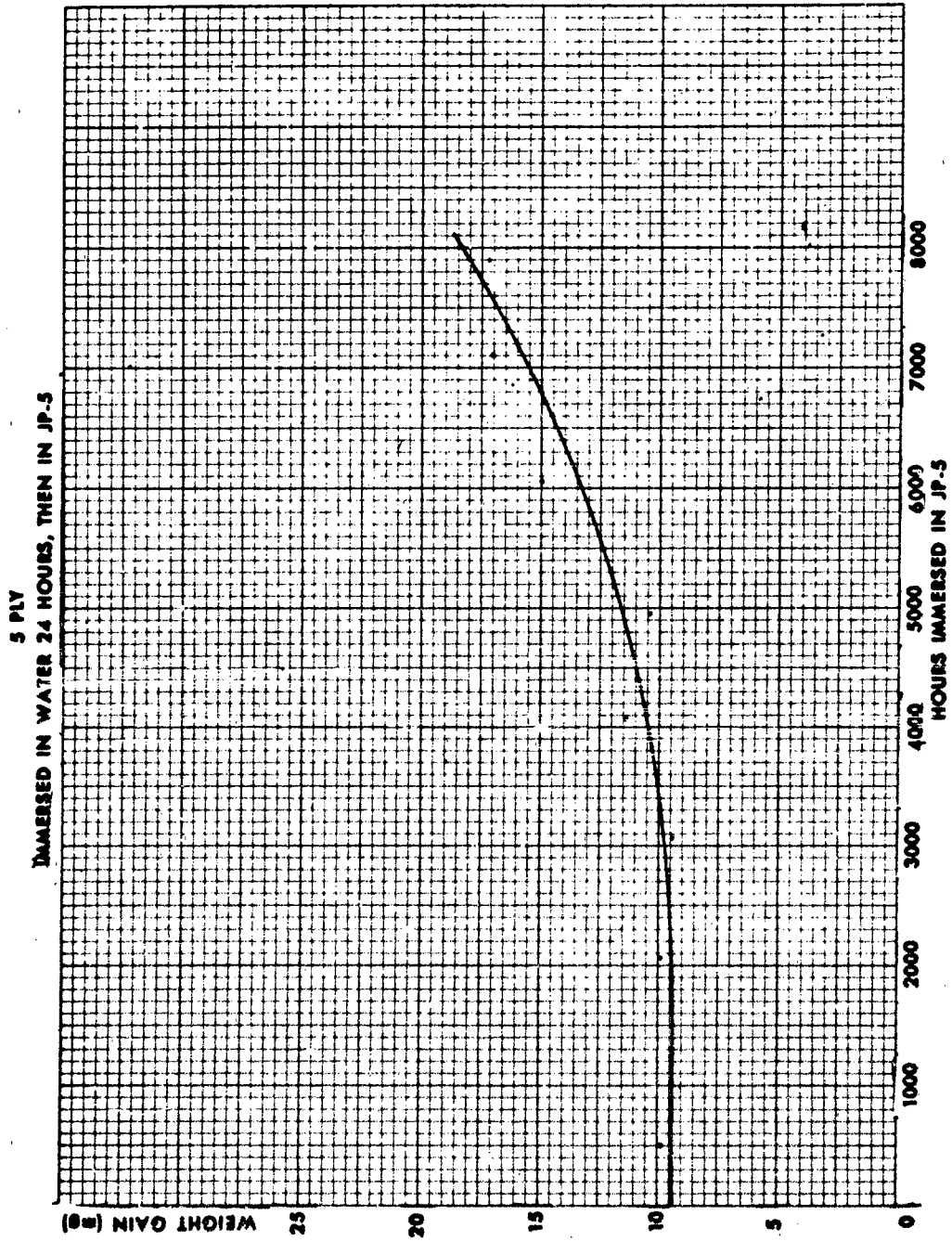


FIGURE 9. 5 PLY CR/E IMMersed IN WATER, THEN JP-5

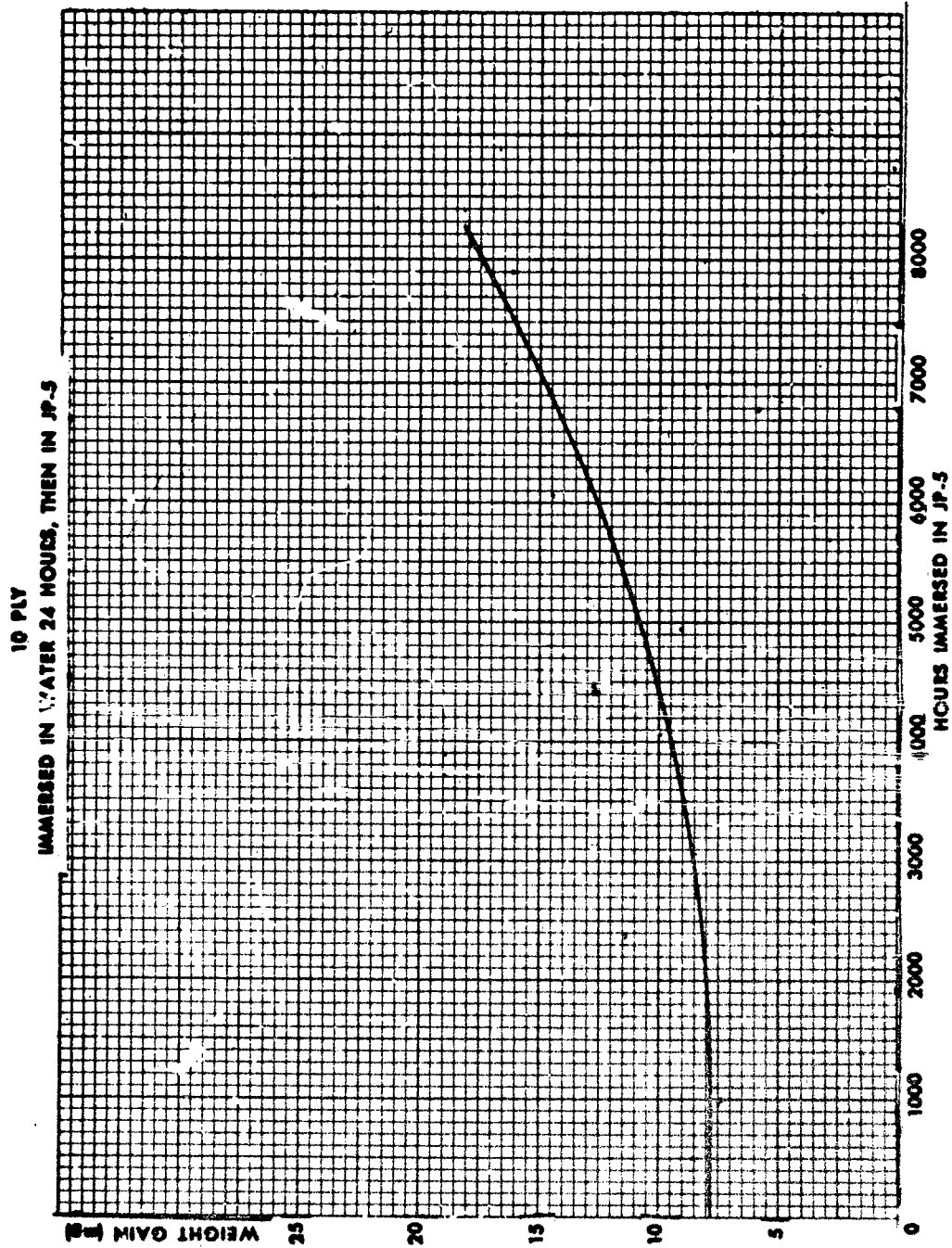


FIGURE 10. 10 PLY CR/E IMMERSED IN WATER, THEN JP-5

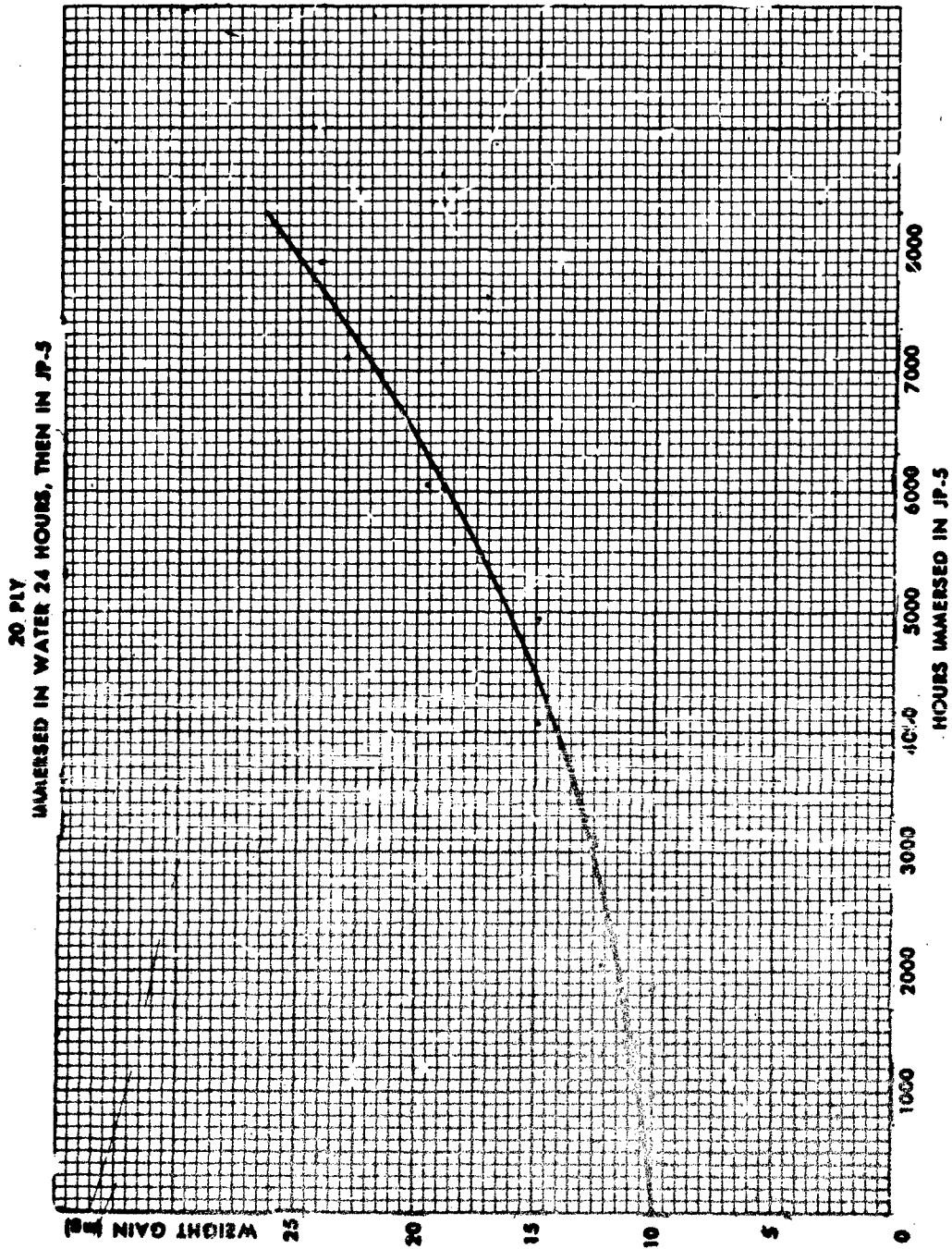


FIGURE 11. 20 PLY GR/E IMMERSED IN WATER, THEN JP-5

TABLE II. FUEL IMMERSION RESULTS

Test Conditions	Number of Plies	At Approximately 5000 Hours				At End of Test			
		Average Original Weight (g)	Average Weight Gain (g)	Avg. Wt. Gain Avg. Orig. Wt.	Avg. Wt. Gain cm ² hr	Duration of Test (Hours)	Average Weight Gain (g)	Avg. Wt. Gain Avg. Orig. Wt.	Avg. Wt. Gain cm ² hr
Immersed in JP-5 Only	5	1.3703	0.0066	4.8×10^{-3}	5.5×10^{-8}	4797			
	10	2.7218	0.0132	4.8×10^{-3}	1.1×10^{-7}	4797			
	20	5.7337	0.0147	2.6×10^{-3}	1.2×10^{-7}	12429	0.0251	4.4×10^{-3}	8.0×10^{-8}
	60	14.4402	0.0115	7.9×10^{-4}	9.5×10^{-8}	12429	0.0238	1.6×10^{-3}	7.6×10^{-8}
Immersed in Water 24 Hours, then in JP-5	5	1.4183	0.0104	7.3×10^{-3}	8.4×10^{-8}	8616	0.0169	1.2×10^{-2}	7.8×10^{-8}
	10	2.3965	0.0091	3.8×10^{-3}	7.3×10^{-8}	8616	0.0171	7.1×10^{-3}	7.9×10^{-8}
	20	5.3095	0.0148	2.8×10^{-3}	1.2×10^{-7}	8616	0.0250	4.7×10^{-3}	1.2×10^{-7}

Area: 25 cm²

All values represent the average of three samples of each ply thickness.

ACKNOWLEDGEMENT

The technical assistance of Myer Perlman is gratefully acknowledged for assembling and monitoring the infrared permeation cell and for the preparation of the infrared spectra used in this study.

REFERENCE

Federal Test Method Standard Number 406, Method 2021, Flammability of Plastics over 0.050 Inch in Thickness, 5 Oct 1961.

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